Preparation of Spherical Monodispersed Titanium Dioxide by Microwave Assistance

Meilong Hu, Chenguang Bai, Mei Song, Xuewei Lv, Shengfu Zhang, Guibao Qiu

College of Material Science and Engineering, Chongqing University, Chongqing 400030, China

hml@cqu.edu.cn

***Abstract*-Spherical Titania (TiO_2) with narrow size distribution and nice dispersibility has been obtained by hydrolysis in the mixed solvent of 1-propanol to de-ionized water under microwave assistance. The results show that the main effects on preparation of spherical TiO_2 with small particle size, narrow size distribute and nice dispersibility include precursor concentration, microwave heating method and pH value. And microwave power has no obvious effect on particle morphology and size distribution.**

Keywords-Microwave Assisted; Spherical Titanium Dioxide; Mono-dispersed

I. INTRODUCTION

In recent years, ultrafine titanium diaoxide particles have been applied to various fields including ceramics [1], optoelectronics [2], catalysis [3], medicine [4], sensor devices [5]， and so on. Parameters like morphology, size distribution，and dispersibility are considered to be much important for titanium dioxide applications. The applications of titanium dioxide are found to be dependent strongly on crystalline structure, morphology, and particle size [6]. TiO_2 has three crystalline phases, namely anatase phase, rutile phase, and brookite phase, which differ in their physical properties, such as refractive index, dielectric constant, and chemical and photochemical reactivity. While rutile phase is a stable phase, anatase phase is preferred for photocatalyst due to its larger band gap (Eg. 3.2 eV compared to Eg. 3.0 eV for rutile) [7]. Anatase phase also is used in graphite, paper-making, and synthetic fibers.

At present, synthesis of spherical TiO_2 particles with narrow distribution has been attached with a lot of attention. Several methods have been developed for generating spherical TiO_2 particles. In industry, TiO_2 powders are produced by sulfuric acid process and chorine acid from ilmenite ore. However, the produced particles are irregular and are in broad size distribution. Spherical TiO_2 with narrow size distribution can be obtained through controlling hydrolysis condition and concentration of the precursor. Barringer and Bowen have prepared TiO_2 spheres with 300-700nm in diameter by controlling the hydrolysis of titanium tetraethoxide in dilute alcoholic solutions [8]. Pal has successfully synthesized titanium dioxide particles of 683 to 50 nm with narrow size distribution through hydrolysis of titanium glycolate in the ethylene glycol [9]. Jiang have produced spherical TiO2 particles of 500-200 nm with narrow size distribution through slow hydrolysis rate of the titanium glycolate [10]. However, synthesis of ultrafine spherical TiO_2 with narrow size distribution and nice dispersibility using inorganic titanium salt is still a challenge.

Recently, with the development of microwave technology, many researchers pay much attention to material preparation under m.0icrowave assistance. It has become a new material synthesis technology, especially in the preparation of nano-materials. For example, Li prepared superparmagnetism of Fe_2O_3 nano-particles by microwave hydrothermal [11]. Li prepared CeO_2 nano-powder with microwave irradiation [12]. Zhu synthesized PAGE-Metal (Ag, Pt, Cu) nano-composite materials by one step in ethylene glycol solution with microwave-assisted [13]. Patra synthesized rare earth phosphate nano-robust with microwave-assisted [14].Yang synthesized CeO_2 nano-particles with microwave-assisted [15]. Nevertheless, it is rare to see report of study on hydrolysis of spherical TiO_2 in microwave field. Heating speed of the microwave is fast and it heats as a whole. Here spherical TiO_2 with narrow size distribution and nice dispersibility is prepared by hydrolysis in mixed solution of 1-propanol and water under microwave assistance by using Ti $(SO_4)_2$ as raw materials. And the best optimum experimental parameters with microwave heating are obtained. Based on these parameters, further experiments will continue.

II. EXPERIMENTAL

At room temperature, we put the mixed solution of 1-propanol and de-ionized water, which volume ratio is 1:1, into single-arch flask and then mix them. Then we measure the pH value of the solution and add appropriate surfactant (PVP) to the mixed solution and shake it up. Finally, we add Ti $(SO_4)_2$ with a certain concentration to the above solution. We put the flask into microwave oven and heat it at a certain microwave power. We stop heating when the solution becomes turbid and we heat it again after several minutes. Several times later we take the flask out of microwave oven when the temperature of the solution decreases at room temperature. We wash solution using the de-ionized water and ethanol. At last, we dry white precipitation for 12 hours, and then we grind and pack it.

Reaction mechanism is as follows, the value of n is determined by the experimental condition.

$$Ti(SO_4)_2 + (2+n)H_2O \xrightarrow{hydrolysis} TiO_2 \bullet nH_2O + 2H_2SO_4$$

$$TiO_2 \bullet H_2O \xrightarrow{condensation} TiO_2 + nH_2O$$

III. RESULTS AND DISCUSSION

A. Effect of Heating Method on Size and Size Distribution

Figure 1 shows the morphology of TiO_2 prepared by hydrolysis of $Ti(SO_4)_2$ at different microwave heating means. Figure 1 (a) is the morphology of TiO_2 with discontinuous heating. Figure 1 (b) shows the morphology of TiO_2 with continuous heating. The results indicated that different heating method has great influence on the properties of hydrolytic products. It may result from the characteristics of microwave heating as a whole. Every part of the solution in the microwave

field can reach hydrolytic temperature in a short time and the whole solution can overcome nucleating potential to nucleation. The variation of supersaturation degree in growth process is shown in Figure 2[16]. With the assistance of microwave field, nucleation can be accomplished in a short time and then grow up. Under discontinuous heating, generated nucleation has enough time to age. Therefore, TiO_2 with narrow particle size distribution and nice dispersibility can be obtained. However, by continuous heating, crystal nucleus does not have enough time to grow up and lead particles to agglomeration.

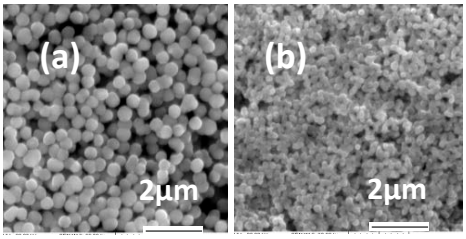

Figure1 SEM images of the prepared TiO_2 at different microwave heating means(a discontinuous heating, b.continuous heating）

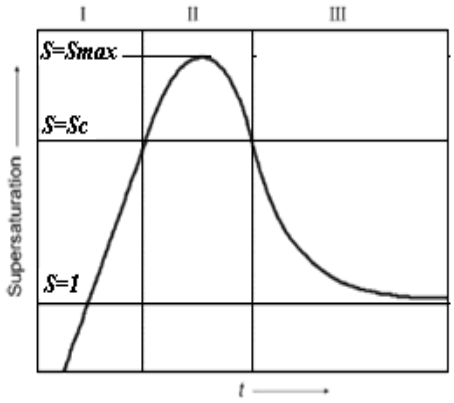

Figure 2 LaMer plot: change of degree of supersaturation as a function of time

Figure 3 is a XRD patterns of prepared TiO_2 by microwave continuous heating, discontinuous heating and roasting at 200 ℃. The sample prepared by continuous heating or discontinuous heating by microwave assisted are brookite TiO_2, while roasting at 200 ℃ is the anatase TiO_2. samples prepared in microwave field must be roasted in high temperature to obtain anatase phase or rutile phase TiO_2.

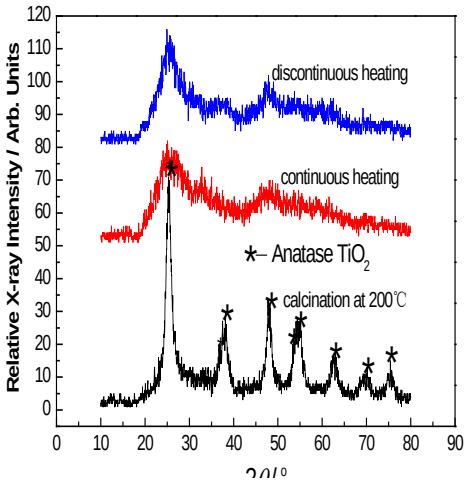

Figure 3 XRD patterns of the prepared TiO2 at different heating methods

B. Effect of Precursor Concentration on Particle Size and Size Distribution

Figure 4 is the SEM images of prepared TiO_2 with different precursor concentration (0.05mol/L, 0.04mol/L, and 0.02mol/L). It indicates that the concentration of Ti $(SO_4)_2$ also has great influence on the morphology of the prepared TiO2. Spherical TiO_2 with small size and narrow size distribution can be prepared when the precursor concentration is low. As Fig. 4(a), when the precursor concentration is high, the prepared TiO_2 sample presents irregular, agglomeration, and wide size distribution. Figure 4 (b) shows that when the concentration is low, the particle size decreased, size distribution narrowed and the particles are spherical. The results were consistent with the preparation of spherical TiO_2 by traditional water bath heating [17]. When PH value keep constant, the temperature of solution increases quickly by microwave, and the solution reached supersaturation in a short time and overcome nucleating potential to nucleation. When precursor concentration is low, Ti $(OH)_4$ can nucleate completely and grow up immediately. When concentration increased, there were some residual Ti $(SO_4)_2$ because of solution supersaturation. Some residual precursor dissolved and some become new nucleation cores. Finally, all those lead that properties of particle such as particle morphology, size distribution, and dispersibility are not better than low precursor concentration.

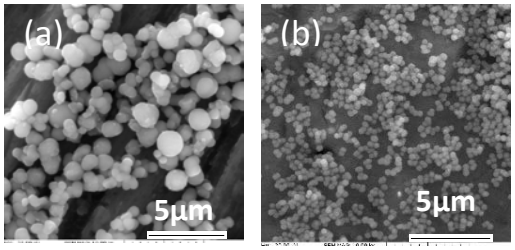

Figure 4 SEM images of the prepared TiO2 at different concentration of the Ti(SO4)2（a:0.05mol/L, b: 0.02mol/L）

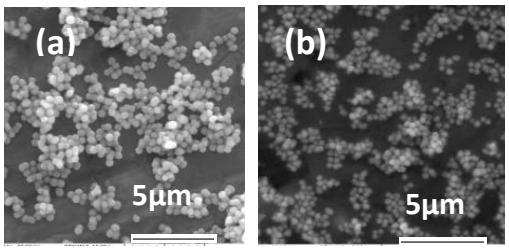

Figure 5 SEM images of the prepared TiO2 at different microwave powers（a.330W, b. 900W）and grain diameters by Lorentzian fitting

C. Effect of Microwave Power on Particle Size and Size Distribution

Figure 5 shows SEM images of TiO_2 samples prepared in different microwave power. Spherical TiO_2 with narrow size distribution and nice dispersibility can be prepared at different microwave powers. Microwave power only influences particle size. As Fig. 5(b) shows that, small size particles are obtained at high microwave power. As Figure 5(a) and Figure 5(b) show that big size particles are obtained at low microwave power. The main reason is that solution can get a fast heating rate at high microwave power and precursor can be hydrolyzed in a short time. The relationship between quantity of crystal nucleus and delivery of precursor solute presents a positive correlation according to nucleation mechanism [19], so particles have small

size and a large amount in high microwave power. However, the opposite situation presents in low microwave power.

Figure 6 shows the TG-DSC curve of prepared sample dried at 80℃. It can be seen that there is a distinct mass loss area before 200℃, and there is a distinct endothermic peak in this area which is caused by physical absorption water removal. Between 200～480℃, there is a mass loss as well, which is caused by losing crystal water. When temperature reaches 500℃, there is a distinct mass loss again which is caused by decomposition of PVP. At 600℃ and 760℃, there is an endothermic peak and exothermic peak, respectively, while the mass has little variation, which is caused by crystal transformation from anatase to rutile. So it indicates that the dried samples should be roasted at 500℃ to obtain TiO2 with high purity and samples should be roasted between 600～760℃ to get anatase TiO2 and get ruitle TiO2 roasted at a higher temperature more than 760℃.

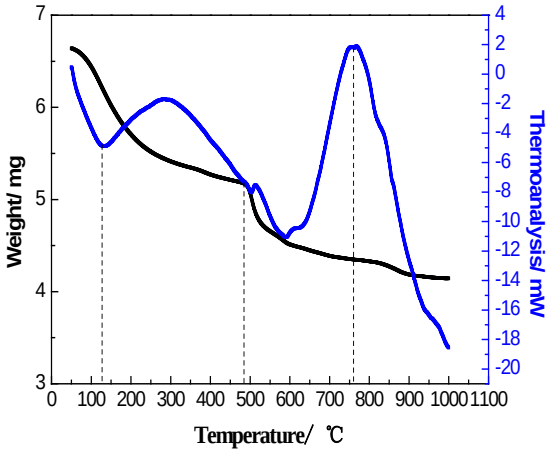

Figure 6 TG-DSC curve of the prepared TiO2

IV. CONCLUSION

By hydrolysis under microwave field and by using commercial $Ti(SO_4)_2$ as raw material, spherical TiO_2 with narrow size distribution and nice disipersibility can be prepared in the mixed solution of 1-propanol and de-ionized water, the volume ratio of which is 1:1. The precursor concentration and microwave heating method have great influence on particle size and size distribution. Low precursor concentration and discontinuous heating are benefited for preparation of spherical TiO_2, while microwave power has no obvious influence on TiO_2 morphology. And different phases TiO_2 can be obtained at different temperature calcined.

REFERENCES

[1] LEE Young Il, LEE Jong-heun, HONG Seong-hyeon, KIM Doh-yeon, "Preparation of nonostructured TiO_2 ceramics by spark plasma sintering," Materials research bulletin, 38, p. 925-930,2003.

[2] TANG Zhi-yong, A.KOTOV Nicholas, GIERSIG Michael, "Spontaneous organization of single CdTe nanoparticles into Luminescent nanowires," Science, vol. 297, p. 237-240, 2002.

[3] CAMPBELL Chartes T., PARKER Stephen C., STARR David E, "The effect of size-dependent nanoparticle energetic on catalyst sintering," 298, p. 811-814, 2002.

[4] EMERICh D F, THANOS C G, "Nanotechnology and medicine," Exp. Opin. Biol. Ther, .3, p. 655-663, 2003.

[5] ZHU, Y. F, SHI J. J, ZHANG, Z Y, ZHANG, C, ZHANG X R, "Development of a gas sensor utilizing chemiluminescence on nanosized titanium dioxide," Analytical Chemistry, 74, p. 120-124,2002.

[6] WANG, W, GU B, LIANG L, A.HAMILTON W, WESOLOWSKI, D J., "Synthesis of Rutile (α-TiO_2) Nanocrystals with Controlled Size and Shape by Low-Temperature Hydrolysis," Effects of Solvent Composition. J. Phys. Chem. B, 108, p. 14789-14792, 2004.

[7] KAY, A, Gra¨tzel M. "Low cost photovoltaic nodules based on dye sensitized nanocrystalline titanium dioxide and carbon powder," Sol. Energy Mater. Sol. Cells, 44, p. 99-117, 1996.

[8] JEAN, J H, RING, T A, "Nucleation and Growth of Monodisperse TiO_2 Powders in Alcohol Solution," Langmuir, 2, p. 251-255, 1986.

[9] PAL Mou, GARCIA Serrano J, SANTIAGO, P, PAL U, "Size-controlled synthesis of spherical TiO_2 nanoparticles: Morphology, crystallization, and phase transition," J. Phys. Chem. C. 111, pp. 96-102, 2007.

[10] JIANG, X C,MAYERS,B, HEEEICHS, T, XIA, Y N. "Direct synthesis of SE.CdSe nanocables and CdSe nanotubes by reacting cadmium salts with Se nanowires," Adv. Mater, 15, p. 1740-1743,2003.

[11] LI Dong-mei, XU Gang-liang, XIONG Kun, et al. "Preparation of superparamagnetic Fe_3O_4 nanoparticle by microwave hydrothermal method," Chemical Engineering Progress, 27, p. 1056－1060, 2008.

[12] LI Sheng-ying, XU Fei, WANG Yun-hong, et al. "Preparation and Characterization of CeO_2 Nanopowders under Microwave Irradiation". Chinese Rare Earths, 28, p. 112-114, 2007.

[13] ZHU, J F, ZHU, Y J. "Microwave-Assisted One-Step Synthesis of Polyacrylamide-Metal (M = Ag, Pt, Cu) Nanocomposites in Ethylene Glycol," J. Phys. Chem.B, 110, p. 8593-8597, 2006.

[14] PATRT, C R, ALEXANDRA, G, PATRA, S, et al. "Microwave approach for the synthesis of rhabdophane-type lanthanide orthophosphate (Ln = La, Ce, Nd, Sm, Eu, Gd and Tb) nanorods under solvothermal conditions," New J. Chem, 29, p. 733 -739, 2005.

[15] YANG, H M, HUANG, C H, Tang A D, et al. "Microwave-assisted synthesis of ceria nanoparticles," Mater. Res. Bull, 40, p. 1690 -1695, 2005.

[16] PARK, J,JIN, J, KWON, S. G, JANG, Y. J, HYEON, T. Angew. "Synthesis of Monodisperse Spherical Nanocrystals," Chem. Int. Ed, 46, p. 4630. 2007.

[17] HU Mei-Long, BAI Chen-Guang, XU Sheng-Ming, XU Gang, LIANG Dong. "Preparation of the Size-Controlled TiO_2 with Spherical Morphology," Acta Phys. -Chim. Sin, 24, p.2287-2292, 2008.